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Progression towards Online Tar Detection Systems

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Abstract

The most prohibitive aspect with the commercialisation of biomass gasification technology is tar fouling of the product gas. The presence of tar impacts the efficiency of gasification systems and compromises gas quality, rendering it less useful for some downstream applications sensitive to gas quality. Various tar detection methods are reported in the literature which can be differentiated into offline and online techniques. However, offline techniques are found to be time consuming, expansive and require sufficient instrumentation and knowledge to achieve reliable results. Recent advances in online tar detection based on spectral information of individual tar component have attracted much research attention. Among these, fluorescence spectroscopy is a highly promising technique for the provision of distinctive, non-invasive and real time data collection for tar levels which can be easily installed on gasification product gas streams. This paper presents the initial work on developing a low cost tar detection system based on LED induced fluorescence. The detection system mainly consists of a photomultiplier tube (PMT), LED (emission wavelength of 280 nm) and 300 nm longpass colour glass filter. Initial experiments have been carried out with different concentrations (0 to 100 wt%) of phenol (used as a model tar compound) and bio-oil samples from an in-house, downdraft (throated) fixed bed gasification system. The results show a linear increase of fluorescence with phenol and the gasifier bio-oil at different concentrations.

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Keywords: Biomass; gasification; tar; fluorescence spectroscopy; online measurement; tar detection

1. Introduction

Global progression of gasification technology is, at least in part, hindered by tar formation and costly tar removal strategies. Excessive tar fouling diminishes gasification efficiency and without expensive scrubbing equipment to eliminate the problem it can lead to downstream complications such as choking and damaged components, requiring periodic cleaning or replacement. Tar detection is a complex and expensive task due to a variety of biomass feedstocks operating under different process conditions and in different gasification systems. Typical offline detection methods (e.g. European tar protocols) are very time consuming, unwieldy and restricted

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to offline use only [1]. Moreover, the intricate nature of tar mixtures, involving a vast number of species with differing polarity, structure and molecular mass, means that aged samples tend to re-polymerise [2]. To avoid some of the drawbacks of the offline methods, some efforts have been made to develop online tar detection systems. These methods are mainly based on Photo Ionization Detection (PID) [3], Ion-Molecule Reactions Mass Spectrometry (IMR-MS) [4], Time-Of-Flight Mass Spectrometry (TOF-MS) with laser ionization [5], Molecular Beam Mass Spectrometry [6], Laser Induced Fluorescence Measurement (LIF) [7] and LED Induced Fluorescence [8]. However, these systems are still underdeveloped and a lot of research is still needed to make reliable, accurate and cost effective measurements when compared to conventional (offline) detection systems.

This research work focuses on the development of low cost tar detection system based on LED induced fluorescence with subsequent instrumentation and control to collect and process the data to alter the state value of the gasifier e.g. equivalence ratio. This paper reports on the initial steps to develop an online tar detection system that can measure the tar concentration within the product gas at high temperature (>350 °C) and in real time. For the sake of easiness and simplification, the system was initially tested offline using model tar compounds in the liquid phase. The system for online tar measurements in the product gas has been fabricated and is currently being installed within an in-house, downdraft, fixed-bed gasification system. The design of the fluorescence system is discussed, followed by some results on using the system on liquid tar samples.

1.1. Biomass gasification tar products

Tars produced from biomass gasification are characteristically complex, rendering detection and measurement within the gas phase a complicated challenge. The definition of tar varies throughout industry and literature. Tar can be regarded as thermal or partial oxidation products which are assumed to be chiefly aromatic compounds with a higher molecular weight greater than Benzene [1]. Lower molecular weight compounds such as Ethylene and Benzene can similarly prove disruptive so shall be classified as tars for the purposes of this research [1, 9]. Tars carried by a product gas stream may choke up pipework leading to blockages and system failures and component damage. Moreover, tars are generally oxygenated and cannot be converted into valuable products and the presence of tars and impurities reduces the useable output syngas, diminishing gasification efficiency and energy potential. Ultimately, the performance of a gasification system, in terms of tar production level, is influenced by the acceptable tar limits of any intended downstream application. Table 1 details typical tar acceptance limits of various syngas run applications, demonstrating the severe sensitivity of most systems to tar fouling.

Table 1. Tar limitations for syngas applications [1, 10]

Application	Tar acceptance limit (g/Nm^3)
Direct combustion	No limit
Gas turbine	0.05-5
IC engine	50-100
Pipeline transport	50-500
Fuel cells	<1

1.2. Fluorescence spectroscopy

Fluorescence spectroscopy is an effective, non-intrusive, and online analytical strategy which can be exploited for tar detection in biomass gasification. Many aromatic molecules are fluorescent, and fluorescence has been used for numerous disciplines including biological and chemical analysis, combustion techniques and medical applications [8]. Following energy absorption, the intensity of the re-emitted fluorescence radiation is directly proportional to the concentration of the excited species and excitation radiation irradiance. Therefore, measurement of the spectral emission of fluorescence radiation provides an extremely accurate representation of the quantity of a fluorescing species. Efficiently detecting fluorescence radiation from tar within the gas phase is dependent on numerous parameters including the tar load within the gas stream, the optical power output of the light source, the amount of time the detector is exposed to the fluorescence, molecule spatial distributions and efficiencies of irradiation and collection optics. The intensity of fluorescence radiation can be expressed as a function of both the absorbance and the quantum yield of a compound by the following equation derived from the Beer-Lambert Laws of absorption [11]:

$$I_f = j \cdot k \cdot I_o \cdot \Phi_f \cdot [1 - e^{-(\varepsilon(\lambda) \cdot b \cdot c)}] \quad (1)$$

Where I_f represents the fluorescence intensity, j encompasses instrumental factors such as collection efficiency and system geometry, k considers the specific fraction of emissions occurring at the excitation wavelength and the probability of reemission of energy, I_o is the intensity of the incident light from the excitation source at the sample, Φ_f is the fluorescence quantum yield, $\varepsilon(\lambda)$ is the molar absorptivity of the molecule, b is the cell path length and c is the concentration. If the value for $\varepsilon(\lambda) \cdot b \cdot c < 0.05$ then equation 1 can be modified to equation 2.

$$I_f \sim j \cdot k \cdot I_o \cdot \Phi_f \cdot \varepsilon(\lambda) \cdot b \cdot c \quad (2)$$

This represents a linearly proportional relationship between the fluorescence intensity emitted from a molecule and concentration. Following the successful design of a tar detection system the principles outlined would enable the development of a control system extrapolating tar concentration data from detected intensity. Correlating the system conditions with computed and measured tar concentrations allows gasifier control strategies to be developed.

2. System Design

The fundamental specifications for the tar detection system are: inexpensive and easily interchangeable components, modest size, transportable and adaptable, robust and secure housing, maximum fluorescence detection efficiency, minimal background interference, precisely aligned and mounted components, components appropriate / sufficiently shielded for high temperature environments. The aspects considered for the following design include excitation, optical filtration, system integration and operation. The design incorporates a 1 mW 280 nm OPTAN LED from Thorlabs which allows for low cost, precise excitation. A 300 nm longpass colour glass filter from Edmund Optics is used to isolate fluorescence radiation. For detection, a highly sensitive R11558 side-on type photomultiplier tube and C4900 HV power supply from Hamamatsu (Japan) are used, providing $1x10^7$ gain for discrete signal capture. The instrumentation is housed in a die-cast aluminum enclosure to provide electromagnetic and heat shielding during operation. An electronic circuit was developed in-house to provide a constant supply voltage and current from a 15 V AC power supply to power both the LED and the high voltage C4900 voltage supply for the photomultiplier tube. The circuit comprises potentiometer voltage control of the input voltage across the photomultiplier, allowing for the optimal voltage to be established before output saturation occurs. The arrangement of the optics and the system for offline liquid phase testing is shown in Figures 1a and 1b, respectively. A custom designed stainless steel optical viewport comprising four optical entry points was made for multidirectional optical access. The custom designed optical cell, attached via a threaded connection and compression fittings to the sample line of the gasifier is shown in Figure 2. The design is a 100 mm x 70 mm x 70 mm block with a 13mm through bore (to match the ID of the outlet pipe of the gasifier hot gas filter).

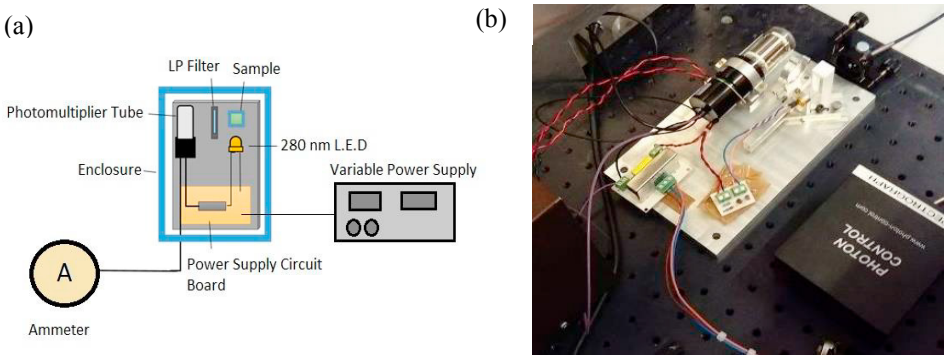

Fig. 1. (a) Instrumentation arrangement schematic for liquid phase testing and (b) picture of system set up

The cell is made from stainless steel (grade 316) to allow for high operating temperatures, material strength, and hardness so as not to be affected by creep loads and abrasive wearing from any particles transported in the product

gas. On each side of the block there is a 12 mm bored through the centre of the block to provide optical access from each side to the cell centre, as well as a shallow 3mm deep, 25 mm diameter bore to seat a quartz window on each side. Each of the windows is flanged with a high temperature gasket material and four separately machined square filleted flanges (each 50 mm x 50 mm x 15 mm). The design is intended to allow excitation from the top window via a mounted LED. As can be seen in Figure 2(a) a small metallic mount is mechanically fastened to the top of the sell to securely and precisely align and hold the LED in place and the output radiation is directed through the centre of the gas sealed quartz window. The bottom side of the cell will incorporate a beam dump to absorb the LED radiation and mitigate scattering. The tar detection system, housed in an aluminium enclosure and mounted on a removable aluminium plate is attached via a mechanical coupling to the side of the optical cell wall using threaded bolt fasteners which screw into the face of the cell. The opposite side is then free for optical access for another spectral detection device such as a spectrometer or CCD camera. Figure 2(b) displays the CAD design for tar detection system connected to the gasifier.

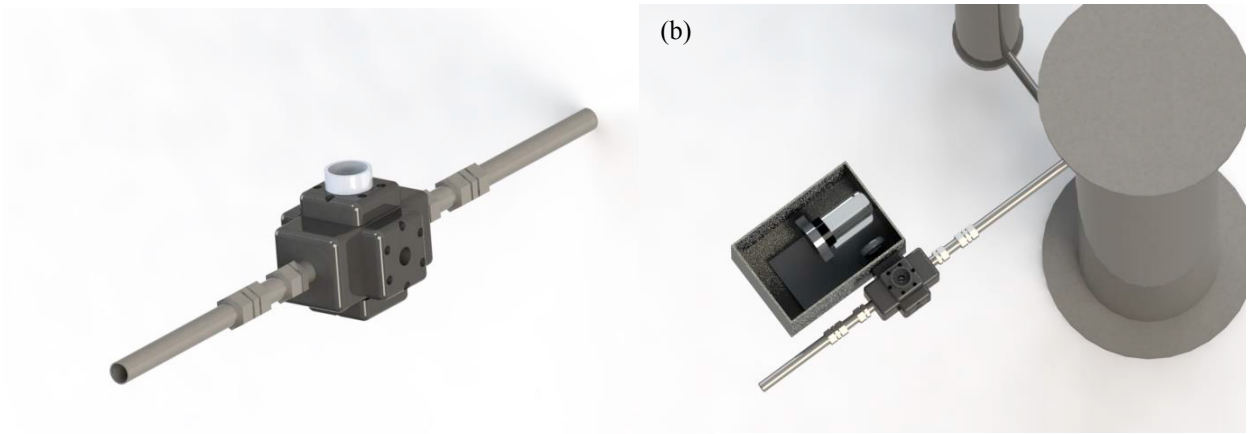

Fig. 2. Online tar detection system (a) custom optical cell design and (b) integration with gasification system and instrumentation housing.

3. Design Validation

The performance of the fluorescence system was evaluated off-line to prove that the specified instrumentation and optics were appropriate for the measurement of fluorescence and to evaluate performance and identify problems before connecting it to the gasifier. Preliminary, testing was conducted in the liquid phase. The following results shows the testing with solutions of known concentration of phenol and samples of bio-oil/tar which were collected from the gasifier and their fluorescence signature investigated.

3.1 Methods

Various phenol solutions were prepared using water as a solvent. For the phenol tests, a total of 10 solutions of increasing concentration were prepared from 8% w/w phenol concentration up to the purchased solution concentration of 80% w/w concentration. The phenol solutions were transferred to a UV quartz cuvette using a pipette (100 - 1000 µL Finn Pipette, Thermoscientific, United States). Once filled and sealed, the cuvette was gently shaken to ensure mixing. For calibration purposes, a sample of water was tested to establish the output observed from the system with no tar or aromatic compounds in the cuvette. Measurements were taken in triplicate. Six separate samples of varying tar concentrations were produced from the samples collected from the gasifier, ranging from 1:5, 2:4, 1:1, 4:2, 5:1 (oil:water). Similarly, the fluorescence was measured after the gentle shaking procedure, which was repeated in triplicate for each sample.

4. Results and Discussions

The results are shown in Figure 3 and clearly show that the fluorescence increased (i.e. more negative) with phenol concentration, and the light detected was lowest for the water only sample. The results presented an almost linear increase of fluorescence with phenol concentration. These results are indicative of the linearly proportional relationship previously identified for fluorescence analysis of phenol within a gas stream. It is worth noting that at the highest concentrations of phenol (64 to 80% w/w) the output was higher (i.e. less negative) than for 56% w/w (which was the most negative output intensity observed during the tests). This is most likely due to inconsistencies with alignment during the setup. The process required removing the cuvette, filling with the

solution and shaking before placing back within the system. This may have led to inconsistencies and any deviations from linearity with the exact positioning of the samples to be measured and may explain the change in the trend. The test results for the gasifier bio-oil experiments shown in Figure 3, similarly show that when a higher percentage of bio-oil is present within a sample the output from the PMT decreases, signifying more intense fluorescence signal.

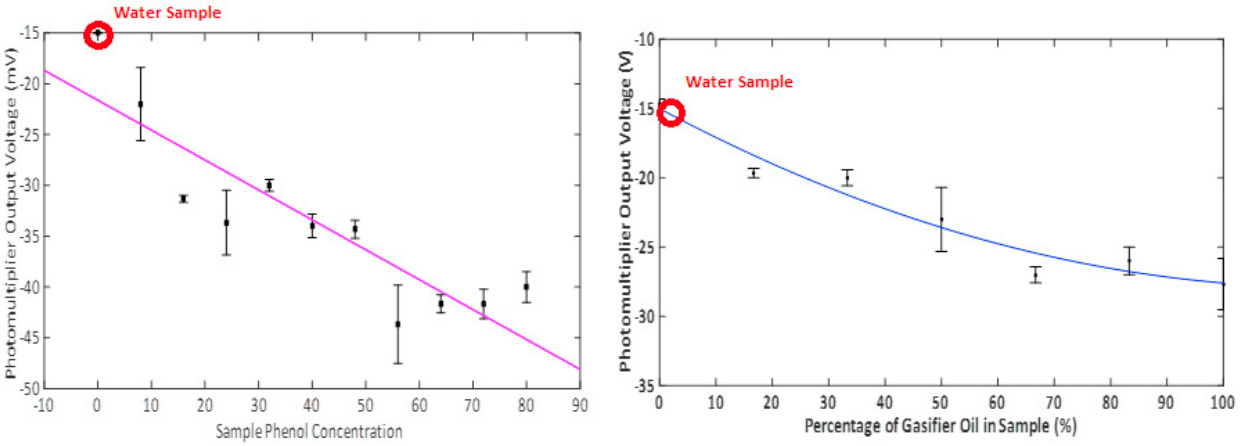

Fig. 3. Spectral response from PMT for varying concentrations of Phenol (left) and bio-oil samples

5. Conclusions

The utilization of fluorescence strategies using LEDs for analysis of tar content seems to be a very promising route for biomass gasification due to the potential for real-time, non-intrusive monitoring. The use of LEDs has been proven to be effective for the stimulation of measurable fluorescence signals in the liquid phase both with a standard tar compound (phenol) of known concentrations and for bio-oil samples derived from a gasifier test using *Miscanthus* biomass. Although exact information regarding the species of tars presents within the bio-oils is unknown, this method demonstrates the components selected could effectively be utilized within a tar detection system for quantitative evaluation of tar loading on a gas stream if coupled with a suitable offline technique, such as the European Tar Protocol, for calibration. The design presented could be effectively developed to provide quantitative data concerning tar quantity on any scale of the gasifier. Ultimately, the system will require testing in the gas phase to evaluate whether the detector is sufficiently sensitive to detect tar loading concentrations in the gas.

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